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INK JET IMAGING OF A LITHOGRAPHIC PRINTING PLATE

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CROSS REFERENCE TO RELATED APPLICATIONS

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This application is a continuation-in-part of U.S. Application Serial No. 10/774,119, filed February 6, 2004, which in turn is a continuation-in-part of U.S. Application Serial No. 09/941,304, filed August 29, 2001 and a continuation-in-part of Application Serial No. 09/941,323, also filed on August 29, 2001, now U.S. Patent No. 6,523,471, which are, in turn, divisionals of U.S. Application Serial No. 09/566,453, filed May 8, 2000, now U.S. Patent No. 6,315,916. This application also claims benefit of U.S. Provisional Application Serial No. 60/455,836 filed on March 19, 2003.

BACKGROUND OF THE INVENTION

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This invention relates to a process for imaging a lithographic printing plate and more particularly to a process using an ink jet printer to imagewise apply a near infrared absorbing imaging material to a plate coating, exposing the plate to a near infrared emitters, followed by developing the coating.

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In the art of lithographic printing it is generally required that one or more lithographic printing plates be mounted on a printing press. The lithographic printing plate is characterized by having on its printing surface oleophilic ink receiving areas in the form of the image to be printed, and hydrophilic water receiving areas corresponding to the other, non-printing areas of the surface. Because of the immiscibility of oil-based lithographic inks and water, on a well-prepared printing plate, ink will fully coat the oleophilic areas of the plate printing surface and not contaminate the hydrophilic areas. The operating press brings

1 the inked plate surface into intimate contact with an impression cylinder or elastic transfer
2 blanket that transfers the ink image to the media to be printed.

3 Traditionally, a lithographic plate is photographically imaged. The plate substrate is
4 most commonly aluminum, from 5 to 12 mils thick, treated so that the printing surface is
5 hydrophilic, although treated or untreated plastic or paper substrates can also be used. The
6 substrate is coated with a solution of a photosensitive composition that is generally
7 oleophilic. Upon drying, the coating layer thickness is commonly about 1 to 3 microns thick.
8 A printing plate with such a photosensitive coating is called “presensitized” (PS). Both
9 negative and positive working photosensitive compositions are used in PS lithographic
10 plates. In a negative plate, light exposure insolubilizes the coating, so that on development
11 the only parts of the coating that aren’t removed are the light imaged areas. The reverse is the
12 case in a positive plate. Light exposure solubilizes the coating; on development the coating is
13 only removed in the areas that are light imaged. In an image reversal process, a positive plate
14 is “blanket exposed” or “flood exposed”, i.e., the entire plate is light exposed without any
15 intervening mask or other means for imaging, and imaged in a separate step which can be
16 performed before or after the blanket exposure step. By this image reversal process, a
17 positive plate can be negatively imaged. The aluminum substrate can be treated to make it
18 hydrophilic either prior to the application of the photosensitive composition or at the time the
19 non-image areas of the coating are removed in a development step. Such a process in which
20 a pre-coated lithographic plate is prepared for press by removing exclusively either the
21 imaged or non-imaged coating in a development step is called a subtractive process; a pre-
22 coated plate having a coating which is at least partially removed in a development step is
23 known as a subtractive plate.

1 Photosensitive compositions used in positive lithographic plates are well known.
2 They are comprised primarily of alkali soluble resins and o-quinone diazide sulfonic acid
3 esters or amides. In addition dyes or colored pigments, indicator dyes, plasticizers and
4 surfactants can also be present. The ingredients are typically dissolved in organic solvents and
5 are coated onto the substrate. Upon drying a thin film or coating is produced.

6 Alkali soluble resins useful in positive plates are well known and include phenol-
7 formaldehyde resins, cresol-formaldehyde resins, styrene-maleic anhydride copolymers, alkyl
8 vinyl ether-maleic anhydride copolymers, co-or ter-polymers that contain either acrylic or
9 methacrylic acids and poly(vinyl phenol). U.S. Pat. No. 4,642,282 describes an alkali soluble
10 polycondensation product that is also useful as the resin component in positive plates.

11 The o-quinone diazide compounds include o-benzoquinone diazides, o-
12 naphthoquinone diazides and o-anthraquinone diazides. O-quinone diazide compounds
13 useful in positive plates are well known and are described in detail in Light Sensitive Systems
14 by J. Kosar, p.339-352. They are further described in U.S. Pat. Nos. 3,046,118; 3,046,119;
15 3,046,120; 3,046,121; 3,046,122; 3,046,123; 3,148,983; 3,181,461; 3,211,553; 3,635,709;
16 3,711,285 and 4,639,406 incorporated in entirety herein by reference.

17 Such positive plates are sensitive to light in the wavelength range of from about 290
18 to 500nm. When used in the standard manner, photo-exposure causes the alkali insoluble o-
19 quinone diazide of the positive plate to be converted into an alkali soluble carboxylic acid.
20 Upon subsequent treatment with a developer, which is a dilute aqueous alkaline solution, the
21 exposed parts of the coating are removed. The unexposed coating is alkali insoluble, because
22 the o-quinone diazide is unaffected by the developer, and remains on the substrate.

1 Traditionally, lithographic plates are imaged by photographic transfer from original
2 artwork. This process is labor-intensive and costly. Hence with the advent of the computer
3 engendering a revolution in the graphics design process preparatory to printing, there have
4 been extensive efforts to pattern printing plates, in particular lithographic printing plates,
5 directly using a computer-controlled apparatus called a platesetter that is supplied with digital
6 data corresponding to the image to be printed. A platesetter has the capability to supply an
7 image forming agent, typically light energy or one or more chemicals, to a plate according to
8 various patterns or images as defined by digital data, i.e., to imagewise apply an image
9 forming agent. Specially manufactured lithographic plates may be required for certain types
10 of platesetters. Such a combination of a computer-controlled platesetter and the proprietary
11 plates used with them along with developer solutions and any other materials or apparatuses
12 necessary to prepare the plates for printing is known as a computer-to-plate (CTP) system.

13 Heretofore, many of the new CTP systems have been large, complex, and expensive.
14 They are designed for use by large printing companies as a means to streamline the prepress
15 process of their printing operations and to take advantage of the rapid exchange and response
16 to the digital information of graphic designs provided by their customers. Many of the new
17 CTP systems use light sources, typically lasers, to directly image PS plates. But using lasers
18 to image plates is very expensive, because the per-unit cost of the lasers is high and because
19 they require sophisticated focusing optics and electronic controls. If because of the cost only
20 a single laser is used, then time becomes a constraint because of the necessity of raster
21 scanning. There remains a strong need for an economical and efficient CTP system for the
22 many smaller printers who utilize lithographic printing.

1 In recent years, ink jet printers have replaced laser printers as the most popular hard
2 copy output printers for computers. Ink jet printers have several competitive advantages over
3 laser printers. One advantage is that it is possible to manufacture an array of 10's or even
4 100's of ink jet nozzles spaced very closely together in a single inexpensive print head. This
5 nozzle array manufacturing capability enables fast printing ink jet devices to be manufactured
6 at a much lower cost than laser printers requiring arrays of lasers. And the precision with
7 which such a nozzle array can be manufactured and the jetting reliability of the incorporated
8 nozzles means that these arrays can be used to print high quality images comparable to photo
9 or laser imaging techniques. Ink jet printers also are increasingly being used for prepress
10 proofing and other graphic arts applications requiring very high quality hard copy output. Ink
11 jet printers are also scalable to larger sizes inexpensively allowing large format imaging at
12 hitherto low prices.

13 In spite of the large and rapidly growing installed base of ink jet printers for hard copy
14 output, ink jet printing technology is not commonly used in CTP systems. There are many
15 challenging technical requirements facing the practitioner who would design such an ink jet
16 based CTP system as can be seen in the prior art. A first requirement is that the ink jet ink
17 used to image the printing plate be jettable, able to form ink drops of repeatable volume and
18 in an unvarying direction. Further, for practical commercial application, the ink must have a
19 long shelf life, in excess of one year or more. US Pat. No. 5,970,873 (DeBoer et al) describes
20 the jetting of a mixture of a sol precursor in a liquid to a suitably prepared printing substrate.
21 But any ink constituents of limited solubility will render unlikely the practical formulation of
22 a jettable, shelf-stable ink. Similar problems exist in US Pat. No. 5,820,932 (Hallman et al)
23 in which complex organic resins are jetted, and US Pat. No. 5,738,013 (Kellet) in which

1 marginally stable transition metal complexes are jetted. In US 6,187,380 B1 (Hallman et al)
2 and 6,131,514 (Simons), inks comprising acrylic resins such as trimethylolpropanetriacrylate
3 and poly(ethylene-co-acrylic acid, sodium salt), are jetted. While it may be possible to make
4 such a ink formulation work for the purposes of a short term experiment, it would almost
5 certainly clog the nozzles of an ink jet printhead were the ink allowed to remain in the printer
6 for the weeks or more that would be a requirement of practical commercial use.

7 Another requirement is that to be of wide utility, the ink jet based CTP system should
8 be able to prepare printing plates with small printing dots, approximately 50 microns in
9 diameter or smaller, so that high resolution images can be printed. Ink jet printers can
10 produce such small dots, but of those having substantial commercial acceptance, only ink jet
11 printers employing aqueous-based inks are practically capable of printing such small dots.
12 Thus the systems described in US Pat. Nos. 4,003,312 (Gunther), 5,495,803 (Gerber),
13 6,104,931 (Fromson et al), and 6,019,045 (Kato) which use solvent-based hot melt inks will
14 not allow the preparation of the high resolution printing plates necessary for printed images
15 of high quality. Further, hot melt type inks typically freeze on top of the imaged media rather
16 than penetrate into it. This would prevent intimate mixing between potential reactants in the
17 inks and corresponding potential reactants in a PS plate coating. It is also required that the
18 prepared printing plates be rugged, capable of sustaining press runs of many thousands of
19 impressions. The waxes used in the hot melt inks described in US Pat. No. 6,019,045 (Kato)
20 and 4833486 (Zerillo) would wear out in such a long press run.

21 Another requirement of a successful ink jet based CTP system is that a mature plate
22 technology is to be preferred. Although the prior art demonstrates that it is not obvious to do
23 so, it greatly simplifies the development of an ink jet CTP system to be able to use

commercially available, widely accepted PS plates. There are many tradeoffs in the manufacture of commercially practical lithographic plates. They must be highly sensitive to the imaging process and yet thermally stable, stable in high humidity storage environments and yellow light, resistant to fingerprints, of minimal toxicity and environmentally benign, easily developed in that small dots are quantitatively resolved without dot blooming using developers that are of minimal toxicity and environmentally benign, able to sustain long press runs, manufacturable at a low cost per square foot, and many other practical requirements. US Pat. No. 5,695,908 (Furukawa) describes a process for preparing a printing plate comprising a new plate coating containing a water-soluble polymer that becomes water-insoluble in contact with a metal ion in a solution jetted imagewise. But such a new plate coating is unlikely to meet the wide array of constraints on a successful plate technology. U.S. Pat. No. 5,466,653 (Ma et al) describes a plate coating that requires an impractically high reaction temperature for imaging. US Pat. No. 6,025,022 (Matzinger) describes a new plate coating on a glass substrate that would be unlikely to find wide acceptance

To use an ink jet printer in a positive imaging process is impractical because in typical printing, the area of a plate containing images such as text, graphics, and line work, is much less than the non-image containing area of the plate. Thus to be able to image widely accepted positive plates with a negative imaging ink jet process is a unique, surprising, and valuable result.

Positive plates based on o-naphthoquinone diazide sulfonic acid esters can be modified by the incorporation of alkaline materials to obtain image reversal. US Patent No. 4,104,070 describes the use of imidazolines; US Patent No. 4,196,003 describes the addition of secondary and tertiary amines and US Patent No. 4,356,254 describes the addition of basic

1 carbonium dyes to produce image reversal. The sequential steps for this image reversal
2 process are imagewise light exposure, heat treatment, blanket light exposure and alkaline
3 development. Those coatings have never achieved any commercial success, which is
4 attributed to the adverse effect on the properties of the coating by the addition of the alkaline
5 materials. US Patent No. 4,007,047 describes image reversal of a positive resist by a
6 modification of the photoimaging process. After imagewise exposure, the resist coating is
7 subjected to an acid treatment by immersion into a heated acid solution, which after a water
8 rinse and drying steps produces a negative image after blanket light exposure and
9 development.

10 The foregoing discussion of the prior art derives primarily from U.S. Patent 6,691,618
11 in which a process for imaging a lithographic printing plate having a pre-sensitized coating is
12 described in which droplets of an insolubilizing chemical in a solvent carrier are applied to a
13 blanket exposed coating to produce an image.

14 On the other hand, methods also are known for making printing plates involving the
15 use of imaging elements that are heat sensitive or switchable rather than photosensitive. See,
16 for example, U.S. Patent Nos. 6,699,640 and 6,605,407.

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18 SUMMARY OF THE INVENTION

19 The present invention provides a process for preparing lithographic plates for printing
20 by employing an ink jet printhead to imagewise apply a near infrared absorbing material to a
21 coated plate. The plate is then exposed to near infrared emitters which heats the coating only
22 in areas where the fluid is applied and produce a solubility change in the underlying coating.
23 Thereafter, upon subsequent treatment with a developer, an image forms that corresponds to

1 the pattern where the near infrared absorbing material is ink jet printed onto the coating. In a
2 negative working system, the coating is insolubilized where the near infrared absorbing
3 material is applied, and on development those areas remain while the unimaged parts are
4 dissolved. The resulting image plate can then be placed directly on a printing press to
5 produce multiple copies.

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7 BRIEF DESCRIPTION OF THE DRAWINGS

8 Further features and advantages of the present invention will be seen from the
9 following detailed description, taken in conjunction with the accompanying drawings, in
10 which

11 Fig. 1 is a block diagram flow chart depicting a general process of the present
12 invention; and

13 Fig. 2 is a block diagram flow chart depicting a process of the present invention used
14 to image a presensitized printing plate in accordance with one embodiment of the present
15 invention.

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17 DETAILED DESCRIPTION OF THE INVENTION

18 The invention comprises a process for preparing a printing plate for press by
19 imagewise applying a near infrared absorbing imaging fluid to a coated plate, exposing the
20 plate to near infrared emitters, and washing the plate with a developing solution. The near
21 infrared absorbing imaging fluid absorbs energy causing a chemical change the underlying
22 plate coating, making the changed coating insoluble to a developing solution in which the
23 unchanged coating is soluble.

1 More particularly, the present invention enables thermally sensitive coatings to be
2 imaged at a much lower cost than the current method of imaging using digitally controlled
3 near infrared lasers. Referring to the attached Fig. 1, in this invention, the thermally sensitive
4 coatings are imaged by much less costly ink jet printers that have the capability of producing
5 high resolution images comparable to laser imaging. By ink jet printing, a fluid containing a
6 near infrared absorbing material is applied imagewise to a coated plate, followed by placing
7 the coated plate in an oven having near infrared emitters. The coating is heated only in the
8 areas where the fluid is applied which produces a solubility change in the coating. On
9 subsequent treatment with a developer, an image will form that corresponds to the pattern
10 that is ink jet printed onto the coating. In a negative working system, the coating is
11 insolubilized where the fluid is applied and on development those areas remain while the
12 unimaged parts are dissolved. The imaged plate can then be placed on a printing press to
13 produce multiple copies. Alternatively, the imaging fluid may be used in a positive working
14 system.

15 A computer-to-plate system according to the invention preferably comprises an ink jet
16 printer (IJP), an oven having near infrared emitters, and a developing processor. To facilitate
17 accurate imaging of the plate, the paper-handling or substrate-handling subsystem of ink jet
18 printer should have a short, straight paper path. A printing plate is generally stiffer and
19 heavier than the paper or media typically used in commercially available ink jet printers. If
20 the plate fed into the printer mechanism must bend before or after being presented to the
21 imaging print head, then the movement of the plate through the printer may not be as accurate
22 as the media for which the printer was designed. One preferred printer is the EPSON Stylus
23 Color 7600 available from Epson America, Inc., Long Beach, California, has such a short,

1 straight paper path. A platen is preferably placed at the entrance to the paper feed
2 mechanism. The platen preferably has a registration guide rail and supports the plate as it is
3 pulled into the printer by the feed mechanism, facilitating the accurate transport of the plate
4 under the imaging print head.

5 In a preferred embodiment, the IJP used is a commercially available drop-on-demand
6 printer capable of printing small ink drops having volumes no larger than 4 picoliters (4 pl)
7 such as the EPSON Stylus Color 7600 ink jet printer available. However, the great flexibility
8 available to the practitioner in formulating near infrared absorbing imaging materials
9 according to the invention means that a well-performing jettable imaging solution can be
10 formulated such that the print head of almost any ink jet printer will be able to form regular
11 drops with good reliability.

12 The oven required for use in the imaging process in accordance with the present
13 invention may be simple and inexpensive. The oven may be a batch or flow through oven
14 having near infrared emitters such as laser diodes. The emission wavelength of the infrared
15 emitters should be matched to the absorption bandwidth of the near infrared absorbing
16 material contained in the imaging ink. By way of example, compounds having OH and NH
17 groups typically absorb at 2.2-3.2 microns. Most aromatics and olefins absorb at about 3.2-
18 3.3 microns. Aliphatics typically absorb at about 3.33-3.55 microns, while aldehydes,
19 ketones, some organic acids and amides typically absorb in the range of 5.7-6.1 microns.
20 Various laser diodes are available commercially that emit radiation in the above ranges.

21 The coating should be a material whose solubility is changed upon heating. Many
22 coatings are useful in this near infrared imaging process. Preferred coatings include

- 23 1. photo-crosslinkable polymeric and polyazide binders;

- 1 2. resole and novolac resins with a latent bronsted acid;
- 2 3. heat setting monomers and binder resins;
- 3 4. monomers with a heat activated polymerization initiator;
- 4 5. novolac resins with a naphthoquinone diazide sulfonic acid ester;
- 5 6. diazole resins; and,
- 6 7. ablative materials.

7 Preferred infrared absorbing imaging materials useful in the imaging fluids in
8 accordance with the present invention include squarylium dyes such as squarylium dye III,
9 croconate dyes such as croconate blue, phthalocyanine, merocyanine dyes such as
10 merocyanine 540, indolizine, pyrilium, dithiolene, metal complexes, carbon black,
11 phthalocyanine and infrared absorption dyes such as ADS 830 AT (available commercially
12 from American Dye Source, Inc.).

13 For reliable jetting, and so that during idle periods the imaging fluid does not dry out
14 in the ink jet nozzle causing it to clog, a humidifying co-solvent may be added to the
15 insolubilizing fluid. The co-solvent can be a polyhydric alcohol such as glycerin, ethoxylated
16 glycerin, ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene
17 glycol, or trimethylol propane, other high boiling point liquids such as pyrrolidone,
18 methylpyrrolidone, or triethanol amine, other simple alcohols such as isopropyl alcohol or
19 tertiary butyl alcohol, or mixtures of such solvents. When used, the co-solvent would
20 typically comprise 5 to 70 percent of the imaging fluid.

21 While generally not necessary, a dye compatible with the near infrared absorbing
22 imaging fluid may be added to the imaging fluid at a level of a few percent to further enhance
23 the visibility of the latent image. The near infrared absorbing imaging fluid may also contain

1 one or more surfactants or wetting agents to control the surface tension of the ink, enhance
2 jettability, and control spread and penetration of the drop on the coated plate. Suitable
3 surfactants and wetting agents include Surfynol 104, Surfynol 465, Surfynol FS-80, Surfynol
4 PSA-216, Dynol 604, Triton X-100, and similar chemicals or mixtures of similar chemicals.
5 When used, surfactants and wetting agents typically comprise 0.001 to 10 weight percent of
6 the imaging fluid.

7 The near infrared absorbing imaging fluid also may contain one or more biocides to
8 prolong the shelf life of the fluid. Suitable biocides include for example Proxel GXL,
9 Sodium Omadine, Dowicil, GivGuard DXN, and similar chemicals or mixtures of such
10 chemicals. When used, the biocide would typically comprise 0.1 to 3 weight percent of the
11 imaging fluid. If the pH of the imaging fluid is over 10, it is not necessary to use a biocide
12 and this is preferred.

13 A typical formulation for near infrared absorbing imaging fluid in accordance with the
14 present invention comprises:

15	Near infrared absorbing imaging material	98%
16	in a suitable solvent	
17	Surfactant and biocide	2%

18 Imagewise application of the near infrared absorbing imaging fluid onto the plate
19 coating using an ink jet printhead results in a latent image on the plate. To complete
20 preparation for use, it is then necessary to expose the imaged plate to near infrared emitters,
21 and then to use a conventional developing processor. A preferred process configuration is
22 illustrated in Figs. 1, 2 and 4. A coated plate 20 is conveyed first through an imaging station
23 22 where a near infrared imaging fluid is imagewise applied. The plate is then conveyed

1 through a oven 24 having near infrared emitters. The coating is heated only in areas where
2 the imaging fluid is applied, which produces a solubility change in the coating. Then, the
3 plated is conveyed through a development station 26 where an appropriate developing
4 solution is applied to the plate and the solubilized coating removed. The plate is then
5 conveyed through a rinse section 28, and finally, fifth through a drying oven 30. The
6 resulting plate is then ready to be used on a press 34.

7 Alternatively, a positive plate may be prepared by a image reversal process in which
8 the plate is coated with a subtractive coating. A near infrared absorbing imaging fluid is
9 applied imagewise to the coating using an ink jet printer as before. The imaged plate is then
10 conveyed through a oven having infrared emitters, and then through a development, rinse and
11 drying station. The plate is then ready for use.

12 The invention will be further described in connection with the following non-limiting
13 examples.

14 Example 1

15 A infrared absorbing imaging fluid is prepared by dissolving squarylium dye III in to
16 form a near infrared sensitive imaging solution comprising 6 weight % of the fluid. A
17 surfactant (Triton X-100 and a biocide, Proxel GXL) where added in weight amounts of .2%
18 and .3% percent, respectively.

19 The imaging solution is image jetted onto an aluminum plate precoated with a
20 Novolac resin and a naphthoquinone diozide sulfonic acid ester. The image plate is then
21 exposed to an oven having infrared emitters followed by development in an alkaline
22 developer solution of the following composition:

23 Sodium metasilicatepentahydrate 55 grams

1 (from the PQ Corp. under the name Pentabead 50)

2 Aerosol OS Surfactant from Cytec 2.2 grams

3 Water 1000 ml

4 The parts of the coating underlying the imaging solution are insolubilized by heat
5 absorbed by the imaging material. The other parts of the coating are soluble in the developer
6 and are removed. The plate is then washed to remove the developer and any imaging
7 material that was not removed by the developing solution, leaving images on the coated plate
8 that correspond to the images of the early applied near infrared absorbing solution. The plate
9 is then dried.

10 The foregoing is exemplary and not intended to limit the scope of the claims that
11 follow.

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